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BINDING OF PENTAMMINERUTHENIUM(II) RESIDUES TO THE
TRIS(BIPYRAZINE)RUTHENIUM(II) COMPLEX (U) YORK UNIV NORTH YORK
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Binding of Pentaammineruthenium(II) Residues to the
Tris(bipyrazine)ruthenium(II) Cation

By

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in

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<p>A series of $[(\text{NH}_3)_5\text{Ru}]_n^{\text{2n+}}(\text{bpz})_n^{\text{2n-}}$ ($n=1,2$) and $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}_n]^{\text{2+2n}}$ ($n=1,3,6$, bpz = bipyrazine) complexes has been synthesized and characterized by means of electronic spectra, ^1H NMR, cyclic voltammetry and spectroelectrochemistry. The complexes are very stable and inert in aqueous solution. The peripheral pentaammineruthenium(II) groups in the tris(bipyrazine) series exhibit strong absorption bands in the visible, around 490 and 660 nm, ascribed to metal-to-ligand charge-transfer transitions. The attached ions can be reversibly oxidized, with formal potentials of approximately 0.65 V versus NHE, in comparison to 0.52 V for the $[(\text{NH}_3)_5\text{Ru}]_n^{\text{2n+}}(\text{bpz})_n^{\text{2n-}}$ complexes. No evidence of intervalence bands with $\epsilon > 100 \text{ M}^{-1} \text{ cm}^{-1}$ (#19 con'd over)</p>			
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Introduction

Ruthenium(II) complexes of bipyrazine (bpz) are of special interest in coordination chemistry, because of their pronounced photochemical activity and of the existence of six peripheral nitrogen atoms available to bind Lewis acids and transition metal ions.²⁻¹⁰ Recently, we reported a detailed kinetic and spectroscopic study on a series of di-to-heptanuclear tris(bipyrazine)-ruthenium(II)-pentacyanoferrate(II) complexes in aqueous solution.¹¹ In this work, we extend the investigation to a series of pentaamineruthenium(II) derivatives, including the $[\text{Ru}(\text{NH}_3)_5(\text{bpz})]^{2+}$ and $[\{\text{Ru}(\text{NH}_3)_5\}_2(\text{bpz})]^{4+}$ species in solid state and in aqueous solution. Electrochemical and electronic spectroscopic data reveal that the several pentaamineruthenium(II) groups are essentially uncoupled to one another, and to the central ruthenium atom.

Experimental Section

The bipyrazine ligand was prepared by the pyrolysis of the bis(2-pyrazinecarboxylate)copper(II) complex at 270-290°C, under an argon atmosphere, as described in the literature.^{3,12} The solid was recrystallized from toluene, yielding pale yellow crystals, mp 186-190°C. [Lit. 190°C].¹³

The complexes $[\text{Ru}(\text{bpz})_3](\text{PF}_6)_2$ and $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{PF}_6)_2$ were prepared by literature methods.^{2,14} $[\text{Ru}(\text{NH}_3)_5(\text{bpz})](\text{PF}_6)_2$ and $[\{\text{Ru}(\text{NH}_3)_5\}_2(\text{bpz})](\text{PF}_6)_4$ were obtained by reacting 0.20 mmol of bpz with 0.20 or 0.40 mmol of $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{PF}_6)_2$ in boiling acetone (25ml) under an argon atmosphere. After 30 min, the deep purple solution was evaporated to dryness at 55°C under a vigorous stream of argon. The black residue was kept under vacuum for one day, and washed with toluene. The compounds were recrystallized by dissolving in a small volume of 1:1 water-acetone solution, and allowing the solvent to evaporate very slowly under reduced pressure. Anal.

calcd for $[\text{Ru}(\text{NH}_3)_5(\text{bpz})](\text{PF}_6)_2$: C, 15.15; H, 3.33; N, 19.87. Found: C, 14.6; H, 3.2; N, 19.7. Calcd for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\text{bpz})](\text{PF}_6)_4 \cdot \text{C}_3\text{H}_6\text{O}$: C, 11.31; H, 3.62; N, 16.78. Found: C, 11.0; H, 3.6; N, 15.8.

The polynuclear complexes $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}_n]^{2+2n}$ $n = 1, 3$ and 6 , were synthesized by reacting 0.025 mmol of $[\text{Ru}(\text{bpz})_3](\text{PF}_6)_2$ with 0.025, 0.075 or 0.150 mmol of $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{PF}_6)_2$ in boiling acetone (25 ml) under an argon atmosphere. After 30 min, the violet-blue solution was evaporated to dryness, at 55°C , with a vigorous stream of argon. Recrystallization was

carried out as in the preceding examples. Anal. calcd. for

$[\text{Ru}(\text{bpz})_3\text{Ru}(\text{NH}_3)_5](\text{PF}_6)_4$: C, 21.48; H, 2.48; N, 17.74. Found: C, 21.6;

H, 3.0; N, 17.9. Calcd for $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}_3](\text{PF}_6)_8$: C, 12.56; H, 2.76;

N, 16.49. Found: C, 12.7; H, 2.9; N, 15.5. Calcd. for

$[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}_6](\text{PF}_6)_{14}$: C, 7.74; H, 2.92; N, 15.79. Found: C, 8.1;

H, 3.0; N, 15.2.

The electronic spectra in the visible-UV region were recorded on a Hewlett-Packard 8451-A diode-array spectrophotometer. The absorption spectra in the near-infrared region were obtained with a Cary 17 spectrophotometer, with the samples dissolved in D_2O . Nuclear magnetic resonance spectra were recorded on a Varian T-60 spectrometer, at a probe temperature of 33°C . The measurements were made in D_2O , with use of 0.03-0.05 M solutions, after converting the hexafluorophosphate salts into the more soluble chloride form, with tetraphenylarsonium chloride. The chloride salts can also be obtained by dissolving the hexafluorophosphate compounds in acetone, and adding one or two drops of concentrated hydrochloric acid. The chloride salts precipitate almost

quantitatively in the presence of acetone and can be easily separated by filtration. *data were collected in the presence of 0.1 M methanol as internal solvent, and converted to Ru. This scale using 247 nm for CH_3*

Cyclic voltammetry was carried out with Princeton Applied Research Corporation (PARC) instrumentation, consisting of a model 173 potentiostat and

a model 175 universal programmer. A glassy carbon electrode was employed for the measurements in aqueous solution, with use of a conventional Luggin capillary arrangement with a Ag/AgCl (1 M KCl) reference electrode. A platinum wire was used as the auxiliary electrode. The measured potentials were converted to the NHE scale by adding 0.222 V. For the measurements in acetonitrile solutions, a platinum disk electrode was used versus a Ag/Ag⁺ (0.01 M silver nitrate in acetonitrile) reference electrode in the presence of 0.10 M tetraethylammonium perchlorate ($E^0 = 0.503$ vs NHE).¹⁵ For the spectroelectrochemical measurements, the PARC 173 potentiostat was used in parallel with the Cary 17 or HP 8451-A spectrophotometer. A three electrode system was designed for a rectangular quartz cell of 0.030 cm optical pathlength. A gold minigrid was used as a transparent working electrode, in the presence of a small Ag/AgCl reference electrode, and a platinum auxiliary electrode.

Results and Discussion

The electronic spectra of the $[\text{Ru}(\text{NH}_3)_5(\text{bpz})]^{2+}$ and $[\{\text{Ru}(\text{NH}_3)_5\}_2(\text{bpz})]^{4+}$ complexes are illustrated in Fig.1. The absorption bands at 230 and 286 nm also occur in free bpz and are ascribed to internal $\pi \rightarrow \pi_2^*$ and $\pi \rightarrow \pi_1^*$ transitions in the aromatic ligand respectively. The absorption band around 500 nm is assigned to the $\text{Ru}(\pi) \rightarrow \text{bpz}(\pi_1^*)$ charge-transfer (MLCT) transition, in comparison with the spectra of pentaammineruthenium(II) complexes of aromatic N-heterocycles.¹⁶ A second MLCT band associated with the $\text{Ru}(\pi) \rightarrow \text{bpz}(\pi_2^*)$ transition is expected in a cis-bipyrazine metal complex at a wavenumber approximately $8 \times 10^3 \text{ cm}^{-1}$ higher than that of the first one, i.e. around 360 nm. This band was not observed in either species and its absence may be evidence of a trans configuration for these species. The uv $\pi \rightarrow \pi^*$ transition (Table 1) in these species lie at the same energies as in the free (trans) ligand and differ in both position and separation from those obtained for the cis

bidentate species. A summary of the electronic transitions can be seen in Table I. While both the 1:1 and 2:1 species can theoretically exist in two isomeric forms depending upon which bpz nitrogen atoms are involved, the clarity of the NMR and UV/VIS spectra lead one to believe that only one isomer is present in each case. On the basis of minimising steric hindrance, binding only to N(4) is most likely (see labeling in Figure 4), and will be assumed henceforth. Note that neither the ^1H NMR nor the uv spectrum of the 1:1 adduct is consistent with the alternative formulation of this species with a bidentate bipyrazine ligand, i.e. as $[\text{Ru}(\text{NH}_3)_4(\text{bpz})]^{2+}$.

Protonation of the pentaammineruthenium(II)-bipyrazine complexes leads to a bathochromic shift of the $\pi\text{-}\pi^*$ and MLCT bands, with several isosbestic points in the visible and UV region, as shown in Fig. 1.A-B.

Quantitative measurements were carried out rapidly, using freshly prepared solutions, in order to minimize the acid catalysed aquation of the ruthenium(II)-ammines.¹⁷ In 0.01-6 M HCl solutions, a single protonation equilibrium is involved in the complexes. The corresponding $\text{pK}_a = 0.85 (\pm .05)$ for both the mononuclear and binuclear complexes was calculated from the linear plots of pH versus $\log[A - A_i]/[A_f - A]$, where A is absorbance and the subscripts i and f refer to the initial and final solutions, respectively. A slope of unity was observed, in agreement with the single protonation hypothesis.¹⁸ The similar pK_a 's of the mononuclear and binuclear complexes are consistent with protonation at the free N-atom of the coordinated pyrazine ring. This atom is expected to have its basicity increased by the backbonding interactions from the Ru(II) ion. In accordance, the pK_a values of the complexes are higher than that previously reported for the free bpz ligand ($\text{pK}_a = 0.45$).³ The increase in basicity of the peripheral nitrogen atom of the coordinated ring is very small, certainly far smaller than the increase observed in $[(\text{NH}_3)_5\text{Ru}(\text{Pyz})]^{2+}$ (Pyz = pyrazine) when it is protonated (from 0.6 to 2.5)¹⁹ or 2,6-dimethylpyrazine (from 1.94 to

3.70).¹⁸ Possibly the existence of the N=C-C=N framework created in the bipyrazine system, generates an alternate path for delocalisation such that the basicity of the far nitrogen is not greatly enhanced (vide infra).

Approximate values for the excited state pKa's were calculated based on the equation (1) excepting however, that such values are approximate, especially if there is excited state structural distortion, or solvent dipole induced distortion.^{19,20}

$$\text{pKa}^* = \text{pKa}(\text{gs}) + (\nu_1 - \nu_2)/476.5 \quad (1)$$

In the case of the mononuclear complex, $\nu_1 = 20,000 \text{ cm}^{-1}$, $\nu_2 = 17,580 \text{ cm}^{-1}$ and $\text{pKa}^* = 5.9$. In the case of the binuclear complex, $\nu_1 = 19,700 \text{ cm}^{-1}$, $\nu_2 = 17,480 \text{ cm}^{-1}$ and $\text{pKa}^* = 5.5$. The value of pK_a^* is some 2 pK units less than for the pyrazine complex but the difference, $\text{pK}_a - \text{pK}_a^*$ is actually rather larger, in both complexes, for the bipyrazine system than for the pyrazine system (5.05 and 4.65 vs. 3.9 units)¹⁹ but less than the difference (5.95 units) seen with the 2,6-dimethylpyrazine system.¹⁸ This discussion must be tempered with the suspicion that the unprotonated species has a trans bpz group, while, possibly, either of the two protonated species in question, may be cis.

Further protonation of the complexes can be observed in concentrated sulfuric acid; however, accurate measurements were precluded by the rapid decomposition of the complexes.

The electronic spectra of the $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}_n]^{2+2n}$ complexes with $n=1,3$ and 6 can be seen in Fig. 2A-C. The absorption bands around 230, 260, 300, 340 and 440 nm were also observed in the $[\text{Ru}(\text{bpz})_3]^{2+}$ cation. The last two bands were ascribed³ to the $\text{Ru}_c(\pi) \rightarrow \text{bpz}(\pi_2^*)$ and $\text{Ru}_c(\pi) \rightarrow \text{bpz}(\pi_1^*)$ MLCT transitions (subscript c refers to central).

Two additional bands appearing around 490 and 660 nm in the spectra of the polynuclear complexes exhibit intensities which increase with the number of attached $[\text{Ru}(\text{NH}_3)_5]^{2+}$ groups (Table I). The energy difference of $5,300 \text{ cm}^{-1}$ is

comparable to that observed for the MLCT bands of the $[\text{Ru}(\text{bpz})_3]^{2+}$ complex, and these new bands can be assigned to the $\text{Ru}_p(\pi) \rightarrow \text{bpz}(\pi_2^*)$ and $\text{Ru}_p(\pi) \rightarrow \text{bpz}(\pi_1^*)$ MLCT transitions from the peripheral (p) metal ions.

In Fig. 3 one can see two different aspects associated with the presence of free peripheral N-atoms in the $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}_3]^{8+}$ complex. First, the complex can be protonated in concentrated HCl, with a set of four simultaneous isosbestic points, and $\text{pK}_a = -2.1$. This value has been evaluated from the Ho acidity functions for concentrated HCl solutions,²¹ and can be compared with the $\text{pK}_a = -2.2$ of the $[\text{Ru}(\text{bpz})_3]^{2+}$ complex^{3b}. In the presence of concentrated sulphuric acid, further changes are observed in the spectra which seem to indicate more drastic effects in the structure of the complexes. The possibility of decomposition reactions cannot be excluded in this case. The red shifted absorption can be assigned to a transition of the type $\text{Ru}(\text{II}) \rightarrow \pi^*(\text{bpzH}^+)$ as discussed previously.^{3b} The second aspect illustrated in Fig. 3.B refers to the binding¹¹ of $[\text{Fe}(\text{CN})_5]^{3-}$ groups in the $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}_3]^{8+}$ complex. The successive attachment of 1 to 3 pentacyanoferrate(II) groups increase the intensity of the MLCT bands at 490 and 660 nm, with a small bathochromic shift (Table I). The $\text{Fe}(\pi) \rightarrow \text{bpz}(\pi_2^*)$ and $\text{Fe}(\pi) \rightarrow \text{bpz}(\pi_1^*)$ transitions in the series of $[\text{Ru}(\text{bpz})_3\{\text{Fe}(\text{CN})_5\}_n]^{2-3n}$ complexes ($n=1$ to 6) were observed near 500 and 700 nm.¹¹ Therefore, in the mixed polynuclear complexes, these bands should occur superimposed upon those from the peripheral ruthenium(II) ions. The spectrum of the $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}_6]^{14+}$ complex is not modified by the presence of cyanoferrate(II) ions, excluding the possibility that the changes illustrated in Fig. 3.B arise from outer-sphere association. The assignments of the three charge transfer bands in the visible region, described here, are supported by resonance Raman data which will be discussed in detail elsewhere.²²

NMR Spectra ^1H NMR spectra of the $[\text{Ru}(\text{NH}_3)_5(\text{bpz})]^{2+}$ and $[\{\text{Ru}(\text{NH}_3)_5\}_2(\text{bpz})]^{4+}$ complexes are shown in Fig. 4.B-C, in comparison with the spectrum of the free ligand (Fig. 4.A). The NMR peaks at 9.46 ppm and 8.86 ppm in the free ligand have been assigned to the protons H3 and to the pair of protons H5 and H6, respectively. The NMR spectrum of the $[\text{Ru}(\text{NH}_3)_5(\text{bpz})]^{2+}$ complex exhibits an apparent doublet at 9.41 ppm, a singlet peak at 8.83 ppm and a doublet signal at 8.27 ppm, having relative intensities of 2:3:1, respectively. The binding of $[\text{Ru}(\text{NH}_3)_5]^{2+}$ ions to the N-heterocyclic ligands has been reported²³ to produce a shielding effect at the ortho protons (here denoted as H3 and H5), as a consequence of the paramagnetic anisotropy and backbonding interactions which predominate over the inductive effects from the Ru(II) ion. These effects have already been discussed in the literature.^{3,9,11, 23-25} The chemical shifts will depend on the extent of the shielding effects from π backbonding and of the deshielding, inductive effects from the metal ion. Previously,¹¹ the H6 protons shifted upfield, while the H5 protons shifted downfield, but to a lesser extent, upon coordination by the pentacyanoferrate(II) group. Therefore, the apparent doublet at 9.4 ppm in the monomeric pentaammineruthenium(II)-bipyrazine complex can be ascribed to the nonequivalent H3 and H3' protons. The singlet peak at 8.83 ppm is associated with the remote H6, H6' and H5' protons. The new doublet at 8.27 ppm is shifted upfield (shielding), being consistent with the H6 resonance signals. The NMR spectrum of the binuclear complex is shown in Fig.4C. In this case, the pair of H3, H3'; H5, H5' and H6, H6' protons are equivalent and the three resonance signals have the same intensity.

A potential problem in discussing the NMR spectra is the probable presence of structural isomers for certain values of n . Thus, for example, for $n = 2$, two pentaammineruthenium groups may bind to different bpz ligands, or conceivably, to the same bpz ligand. Moreover even where they bind to different

bpz ligands, two isomers exist differing in the relative positions of the pentammine groups. We discuss here the low resolution NMR considering the different types of proton present without considering their relative numbers, which will depend upon the isomer mix.

The methods used to prepare these compounds might be expected to yield a statistical mixture of products. Analytical data suggest but do not provide definitive proof of the unique n value of each species isolated. On the basis of the NMR data reported here ^{and} some preliminary high field NMR experiments, the following statements may be made:

- (i) Mixing of the $n = 1$ and $n = 3$, or $n = 0$ and $n = 6$ species causes no re-equilibration below 50° in water, the mixed (not averaged) spectra being obtained.
- (ii) The $n = 1$ species appears to be a single compound but the presence of some $n = 0$ cannot be ruled out. Higher values of n are absent.
- (iii) The $n = 3$ species spectrum is complex, indicative at least of several $n = 3$ isomers. If $n = 4, 5, 6$ are present, they can only be present in small amount.
- (iv) The $n = 6$ species is not contaminated with $n = 0-3$, but the presence of small amounts of $n = 4, 5$ cannot be excluded at this time. The evidence would indeed favour the isolation of compounds of unique n , as was apparently the case with the pentacyanoferrate(II) species.¹¹ The absence of a statistical mixture is likely a consequence of the kinetic factors controlling the binding of each ruthenium pentaammine residue.

The ^1H NMR spectra of the $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}_n]^{2+2n}$ complexes with $n=0, 3, 6$ are shown in Fig. 5.A-C. For the $[\text{Ru}(\text{bpz})_3]^{2+}$ complex, the resonance signals observed at 10.05, 8.85 and 8.17 ppm were previously assigned to the H3, H5 and H6 protons, respectively. The NMR spectrum of the $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}_3]^{8+}$ complex does not seem to differ appreciably from the spectrum of the $[\text{Ru}(\text{bpz})_3]^{2+}$ cation. Given the close similarity in the spectra

shown in Fig. 5A and B, and the small changes seen in the $\text{bpz}[\text{Ru}(\text{NH}_3)_5]_n$ system ($n=1,2$), with peripheral coordination, the assignment outlined in Table 2 is proposed. Any other assignment requires a substantial downfield shift in H6 or H6' which, again by analogy with the data in Fig. 4, seems unlikely. In the case of the heptanuclear complex, $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}_6]^{14+}$ the resonance signals at 9.96 (singlet), 8.83 (doublet) and 7.65 ppm (doublet) can be ascribed to the H3, H3'; H5, H5' and H6, H6' protons, respectively.

Electrochemistry Cyclic voltammograms of the $[\text{Ru}(\text{NH}_3)_5(\text{bpz})]^{2+}$ and $[\{\text{Ru}(\text{NH}_3)_5\}_2(\text{bpz})]^{4+}$ complexes can be seen in Fig. 6. The voltammograms of the mononuclear complex follow very closely the several reversibility criteria based on the treatment of Nicholson and Shain,²⁶ with $E_0 = 0.52$ V versus NHE and a diffusion coefficient of $2.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. The observed Ru(III)/Ru(II) potential is in the expected region.²⁷ In the case of the binuclear complex, only a single pair of cathodic and anodic waves is observed with a peak separation of 70 mV, and $E_0 = 0.53$ V. The voltammograms for the mononuclear and binuclear complexes normalised to constant [Ru] are shown in Fig. 6 and are very similar; however, the current profile for the binuclear species is broader than for the mononuclear species. As anticipated, the Faradaic current for the bis-ruthenium species, is twice as large as for the mono-ruthenium species. The voltammograms of the binuclear complex can be simulated by a sum of two mono-electronic reversible waves, separated by approximately 0.01 V.

Spectroelectrochemical oxidation of the binuclear species proceeds as shown in Fig. 7.A with a formal potential of 0.52 V, leading to complete decay of the two $\text{Ru(II)}_p \longrightarrow \pi^* \text{ bpz MLCT}$ bands in the visible region. The Nernst slope of 70 mV is slightly higher than that expected for a reversible mono-electronic

process (e.g. 59 mV) and is consistent with the occurrence of two successive steps having very similar E^0 . Measurements of the peripherally oxidised species in the near-ir region (800-1800 nm), in D_2O solutions, provided no evidence of low energy intervalence transfer (IT) transitions with $\epsilon > 100 \text{ M}^{-1} \text{ cm}^{-1}$.

Cyclic voltammograms of the $[\text{Ru}(\text{bpz})_3\text{Ru}(\text{NH}_3)_5]^{4+}$ complex in aqueous solution are shown in Fig. 8.A. The voltammograms are consistent with a reversible mono-electronic process, with $E^0 = 0.69 \text{ V}$ and $D = 2.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. In the cases of the 1:3 and 1:6 polynuclear complexes, a pair of broad, quasi-reversible waves can be observed around 0.7 V in Fig. 8.B.C. The cathodic and anodic peaks are separated by almost 150 mV, having approximately 1:1 intensity ratio. The peak potentials do not vary with the potential scan rates in the range of 20-200 mV s^{-1} . It seems probable that the large separation between the cathodic and anodic waves arises from the superimposition of several parallel mono-electronic processes having very close E^0 values. A quantitative simulation can be made, as in Fig. 8. B, C, by assuming a set of three reversible waves for the 1:3 complex, with $E^0 = 0.67, 0.72$ and 0.77 V , ($D = 2.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$), and a set of six reversible waves for the 1:6 complex, with $E^0 = 0.62, 0.66, 0.70, 0.74, 0.78$ and 0.82 V ($D = 1.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$).

The spectroelectrochemistry of the $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}_3]^{8+}$ and $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}_6]^{14+}$ complexes in aqueous solution is illustrated in Fig. 7.B,C. The oxidation process leads to a decay of the $\text{Ru}_p \rightarrow \text{bpz}(\pi_1^*, \pi_2^*)$ bands in the visible region, indicating that the peripheral $[\text{Ru}(\text{NH}_3)_5]^{2+}$ groups are totally oxidized within a narrow range of potentials around 0.7 V. This result confirms the occurrence of the several parallel steps in the cyclic voltammograms. The spectra can be regenerated in more than 90% and 70% yield for the 1:3 and 1:6 complexes, respectively, by reduction at a

potential just negative of 0.7V. As expected, the corresponding Nernst slopes of 100 and 130 mV differ from that of a reversible mono-electronic process, and are consistent with a series of parallel mono-electronic steps having very close E^0 values.

The electronic spectra of the $[\text{Ru(II)(bpz)}_3\{\text{Ru(III)(NH}_3)_5\}_n]^{2+3n}$ complexes resemble that of the $[\text{Ru(bpz)}_3]^{2+}$ cation, with an additional absorbance increase around 360 nm probably associated with LMCT charge-transfer transitions in the (N-heterocyclic) pentaammine-ruthenium(III) groups.^{28,29}

Spectroelectrochemical measurements in the near-IR region (800-1800 nm), in D_2O solutions, provided no evidence of intervalence bands with $\epsilon > 100 \text{ M}^{-1} \text{ cm}^{-1}$. The possibility that the IT band is associated with the residual absorption around 700-800 nm, observed spectroelectrochemically, cannot be excluded. However, considering that minor, but detectable amounts of decomposed oxidized products are always present in these systems, any assignment would be too speculative at the present stage.

Cyclic voltammograms in acetonitrile solutions are shown in Fig. 9. The quasi-reversible waves associated with the $[\text{Ru(NH}_3)_5] \text{ (III)/(II)}$ couples are similar to those measured in aqueous solution, except for an anodic shift of approximately 200 mv which can be ascribed to solvent effects.²⁷ The several waves observed at -0.5, -0.65 and -0.9 V versus NHE for the $[\text{Ru(bpz)}_3\text{Ru(NH}_3)_5]^{4+}$ complex are similar to those previously reported for the $[\text{Ru(bpz)}_3]^{2+}$ cation,³ and can be ascribed to the successive reduction of the bpz ligands. The electrochemical behavior becomes more complicated in the case of the 1:3 and 1:6 complexes, as shown in Fig. 9.B-C.

However this behaviour is, in part, due to severe adsorption problems.

Concluding Remarks

The polynuclear $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}_n]^{2+2n}$ complexes represent an interesting, cubic symmetry version of the linear array $[(\text{NH}_3)_5\text{Ru}(\text{pzRu}(\text{NH}_3)_4\text{pz})_n-\text{Ru}(\text{NH}_3)_5]^{4+2n}$ ($n=2,3,4$) complexes studied by von Kameke, Tom and Taube.³⁰ However, in contrast with the extended interactions observed in the linear systems, the peripheral $[\text{Ru}(\text{NH}_3)_5]^{2+}$ groups seem to be relatively isolated in the cubic complex. The energies of the MLCT bands and the electrochemical potentials for the $\text{Ru(III)}/\text{Ru(II)}$ couples vary only slightly with the number of $[\text{Ru}(\text{NH}_3)_5]^{2+}$ groups. No evidence of IT bands with $\epsilon > 100 \text{ M}^{-1} \text{ cm}^{-1}$ have been detected in the near IR region, in contrast with the linear pyrazine bridged systems and with Creutz and Taube's ion^{31,32} $[(\text{NH}_3)_5\text{Ru}-\text{pz}-\text{Ru}(\text{NH}_3)_5]^{5+}$. It is evident that up to six pentaamine-ruthenium(II) (or pentacyanoferrate(II)¹¹) groups may be coordinated by the $[\text{Ru}(\text{bpz})_3]^{2+}$ cation and that interaction between these groups is minimal. Surprisingly, the central $\text{Ru(II)}_c \longrightarrow \pi^* \text{ bpz}$ transition is also unaffected by such peripheral coordination, even when all the pentaamine groups are oxidised to Ru(III) . This is contrary to the situation where the bpz rings are protonated,^{3b} in which case there is an effect upon the $\text{Ru(II)}_c \longrightarrow \pi^* \text{ bpz}$ transition energy. Lavalley and Fleischer²³ noted that the MLCT transitions of $\text{LRu}(\text{NH}_3)_5$ species (L = a heterocyclic ligand) were linearly related to the redox potential $E(L/L^-)$ of the ligand L , where reduction occurs into the same orbital into which the electronic transition occurs. If we regard the unit $[\text{Ru}(\text{bpz})_3]^{2+}$ as a ligand towards $[\text{Ru}(\text{NH}_3)_5]^{2+}$, then we may add this datum point to the same graph, using the reduction potential for $[\text{Ru}(\text{bpz})_3]^{2+}$ instead of that for a simple ligand L . This extra datum point lies exceptionally well on the same line as the other ligands L but at very much more positive potential. The equation of this line for 11 points is:

$$\nu(\text{CT}) = 0.51 E(L/L^-) + 1.59 \text{ (in eV)} [R = 0.98]$$

It is surely of considerable interest that the electronic spectra of these species are almost independent of the degree of peripheral binding, that each ruthenium pentaammine (or pentacyanoferrate) fragment is independent of each other, and further that the central ruthenium to bpz MLCT transition is independent of the extent of peripheral binding, even when the $[\text{Ru}(\text{NH}_3)_5]^{2+}$ groups are oxidised to $[\text{Ru}(\text{NH}_3)_5]^{3+}$. Recall that this is not true for binding of protons.^{3b} Expressed in another way, the several $[\text{Ru}(\text{NH}_3)_5]^{2+}$ groups generate several MLCT excited states which do not couple to each other, nor to the central $[\text{Ru}(\text{III})_c(\text{bpz}^-)]$ excited MLCT state, at least on the time scale of absorption. Further, the $[\text{Ru}(\text{III})_p/\text{Ru}(\text{II})_p]$ couples appear identical, except for statistical effects, independent of the number of peripheral groups. Thus the ground state wavefunctions involving these groups are localized on each pyrazine ring. These results have considerable significance with respect to our understanding of the nature of charge transfer states, and their localisation and delocalisation and emission. Possibly each $\text{Ru}(\text{III})_p \longrightarrow \pi^*(\text{bpz})$ transition is located within its own pyrazine ring and the transition is orthogonal to the central $\text{Ru}(\text{II})_c \longrightarrow \pi^*(\text{bpz})$ transition which, possibly, is localised in the diimine framework. Note that such diimine localisation is consistent with the lack of a significant increase in the pK_a value of the nitrogen atom trans to the ruthenium atom in the complexes $\text{bpz}[\text{Ru}(\text{NH}_3)_5]_n$ ($n=1,2$).

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Figure 7

Spectroelectrochemistry of (A) $[\{\text{Ru}(\text{NH}_3)_5\}_2(\text{bpz})]^{4+}$ (1.3 mM) (B) $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}_3]^{8+}$ (1.4 mM) and (C) $[\text{Ru}(\text{bpz})_3[\text{Ru}(\text{NH}_3)_5]_6]^{14+}$ (0.4 mM, in aqueous solution, 0.10 M NaCl, 25°C: (a) 0 (b) 0.48, (c) 0.52, (d) 0.56, (e) 0.70, (f) 0, (g) 0.62, (h) 0.67, (i) 0.72, (j) 0.85, (k) 0, (l) 0.57, (m) 0.62, (n) 0.67, (o) 0.72, (p) 0.90 V vs NHE.

Figure 8

Cyclic voltammograms of the (A) 1:1, (B) 1:3 and (C) 1:6 tris(bipyrazine)-ruthenium(II)-pentaammineruthenium(II) polynuclear complexes, 0.8, 1.0, and 0.6 mM, respectively, in aqueous solution, 25°C, 0.10 M NaCl. Dotted lines refer to tentative deconvolution of the voltammograms in a series of reversible mono-electronic waves, black circles = theoretical values.

Figure 9

Cyclic voltammograms of the $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}_n]^{2+2n}$ complexes with (A) $n=1$, (B) $n=3$ and (C) $n=6$, in acetonitrile (saturated solution) in the presence of 0.10 M tetraethylammonium hexafluorophosphate, 25°C.

Figure Caption

Figure 1

Electronic spectra of (A) $[\text{Ru}(\text{NH}_3)_5(\text{bpz})]^{2+}$ and (B) $[\{\text{Ru}(\text{NH}_3)_5\}_2(\text{bpz})]^{4+}$ (0.05 mM) in (a,d) water (pH 7), (b,e) 0.12 M HCl and (c,f) 3 M HCl.

Figure 2

Electronic spectra of the $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}_n]^{2+2n}$ polynuclear complexes in aqueous solution with $n=1$ (A), 3 (B) and 6 (C), around 0.037, 0.033 and 0.017 mM, respectively.

Figure 3

(A) Electronic spectra of the $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}_3]^{8+}$ complex (0.033 mM) in (a) water (pH 7), (b) 5M HCl, (c) 8 M HCl, (d) 12 M HCl, and (B) in the presence of (e) 0, (f) 1, (g) 2 and (h) 3 equivalents of the aquapentacyano-ferrate(II) ion.

Figure 4

^1H NMR spectra of (A) bpz, (B) $[\text{Ru}(\text{NH}_3)_5(\text{bpz})]^{2+}$ and (C) $[(\text{NH}_3)_5\text{Ru}-\text{bpz}-\text{Ru}(\text{NH}_3)_5]^{4+}$, 0.03-0.05 M in D_2O , 30°C. (Chemical shifts versus TMS).

Figure 5

^1H NMR spectra of (A) $[\text{Ru}(\text{bpz})_3]^{2+}$, (B) $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}_3]^{8+}$ and (C) $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}_6]^{14+}$ 0.03 M in D_2O , 30°C. (Chemical shifts versus TMS).

Figure 6

Cyclic voltammograms of $[\text{Ru}(\text{NH}_3)_5(\text{bpz})]^{2+}$ (...) (3 mM) and $[\{\text{Ru}(\text{NH}_3)_5\}_2(\text{bpz})]^{4+}$ (—) (1.5 mM) at several potential scan rates, in aqueous solution, 0.10 M NaCl, 25°C.

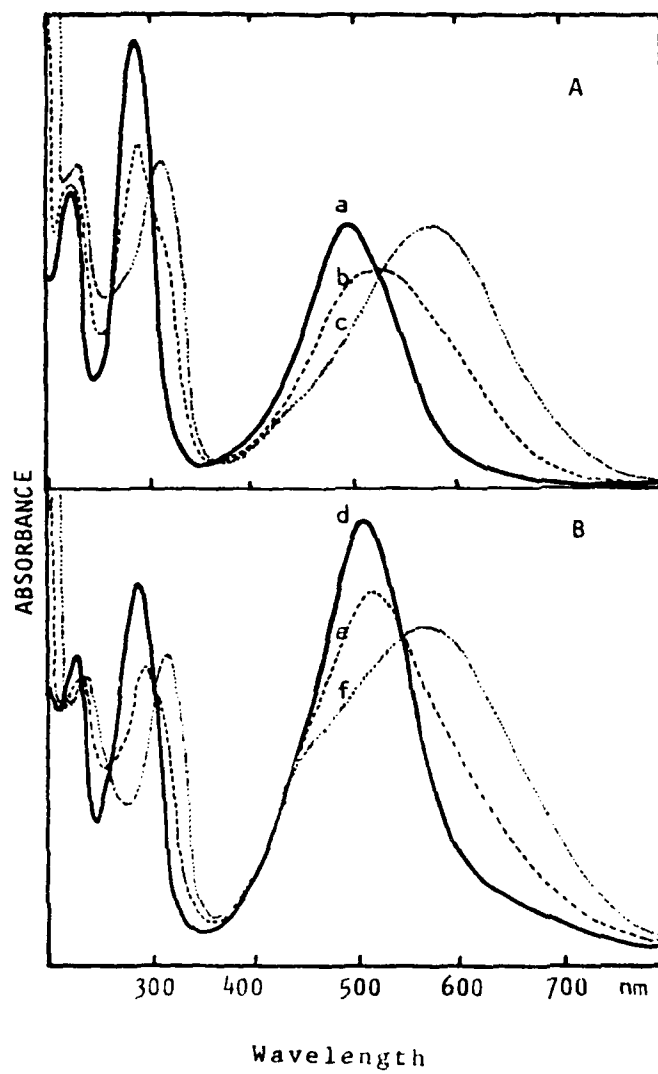


Figure 2

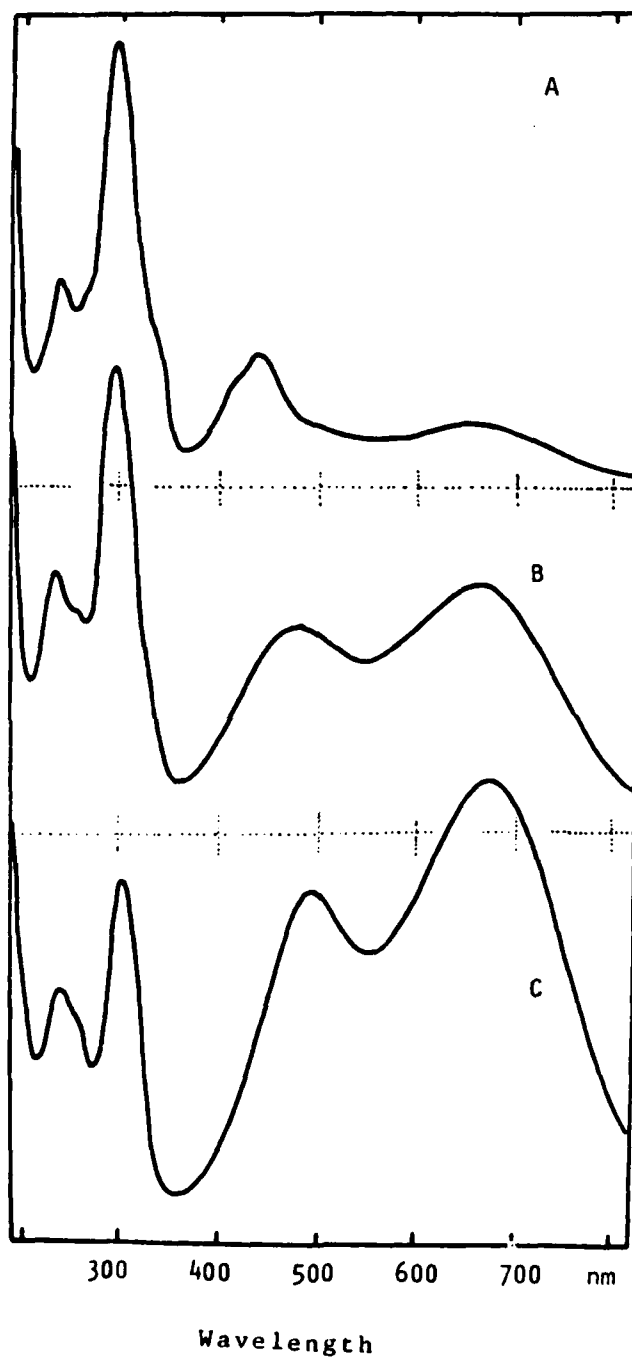
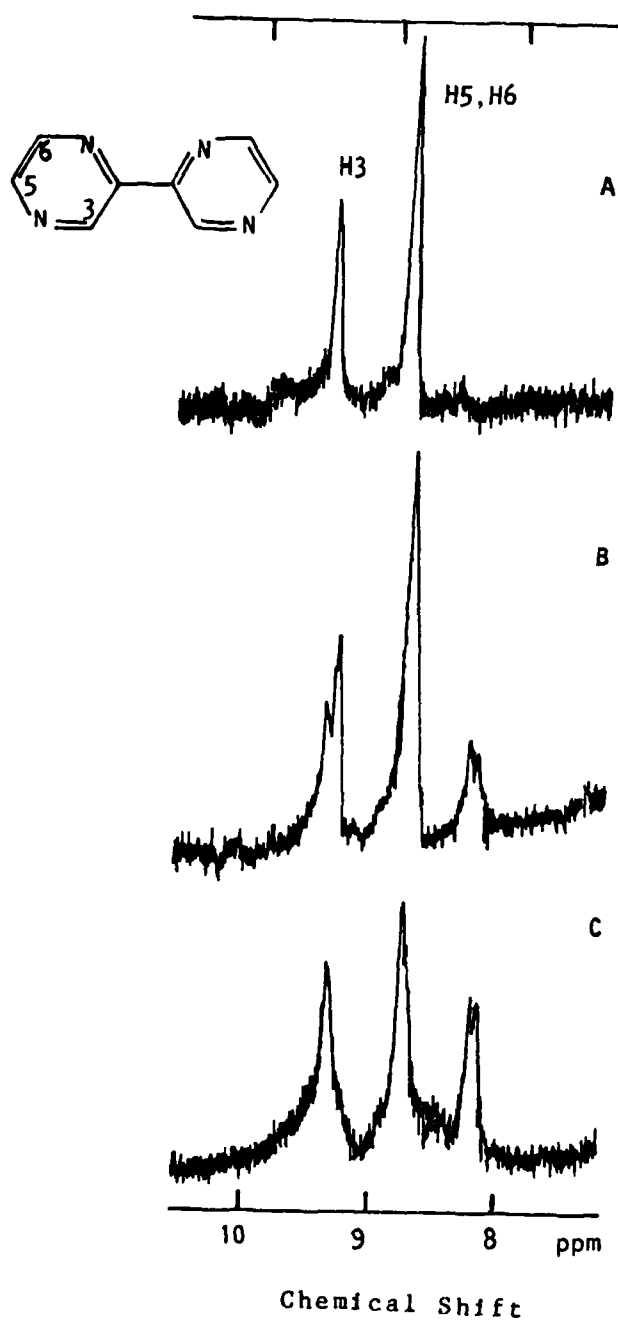


Figure 3



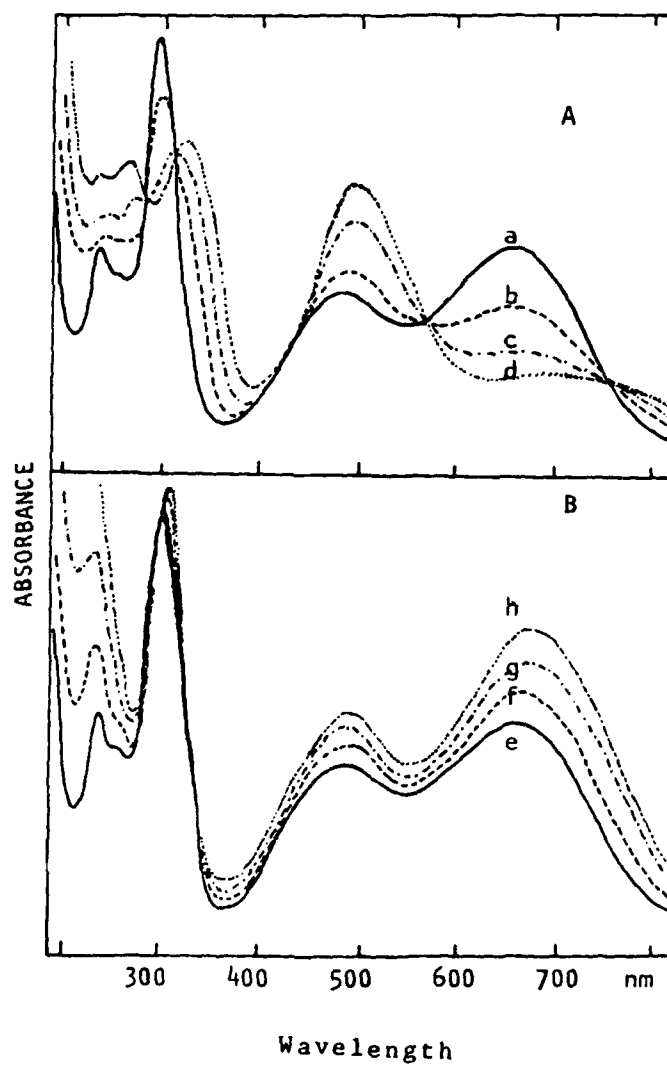


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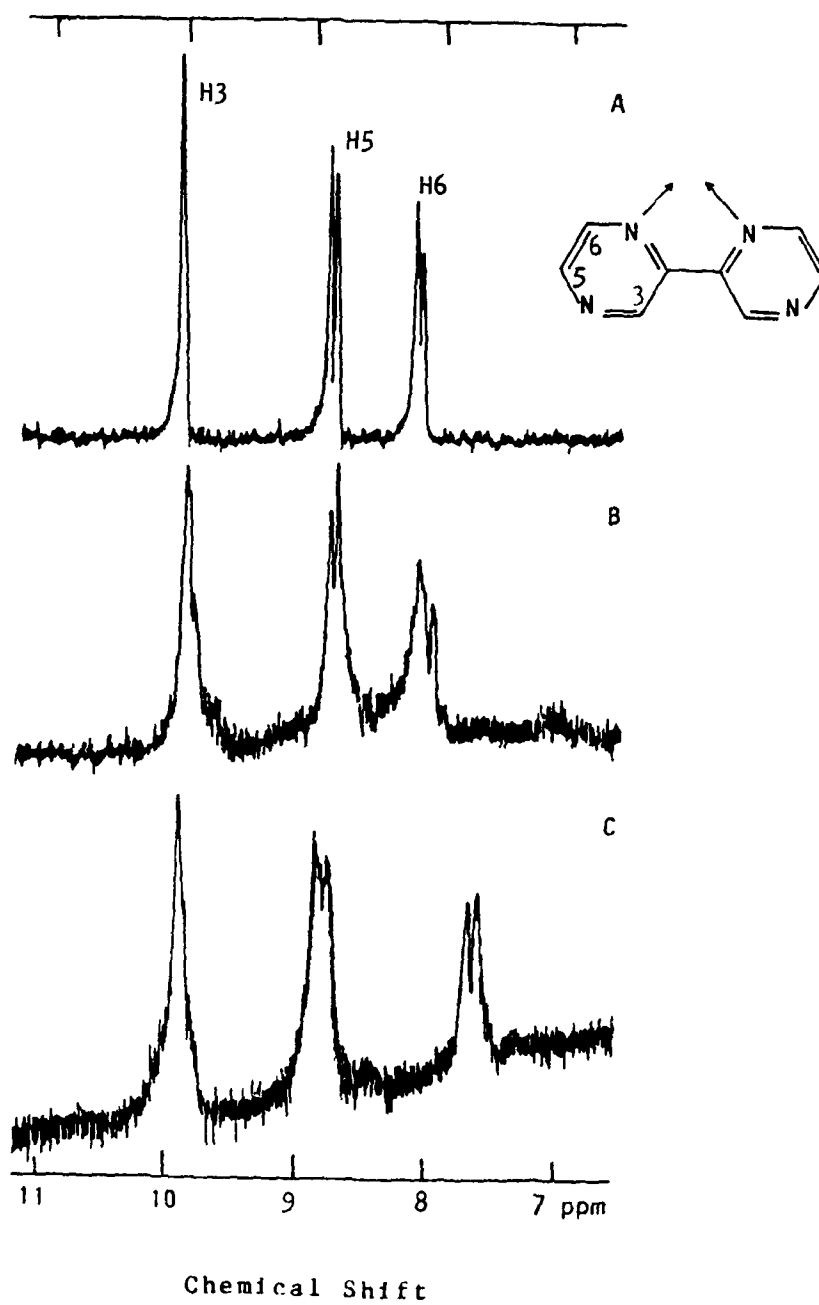


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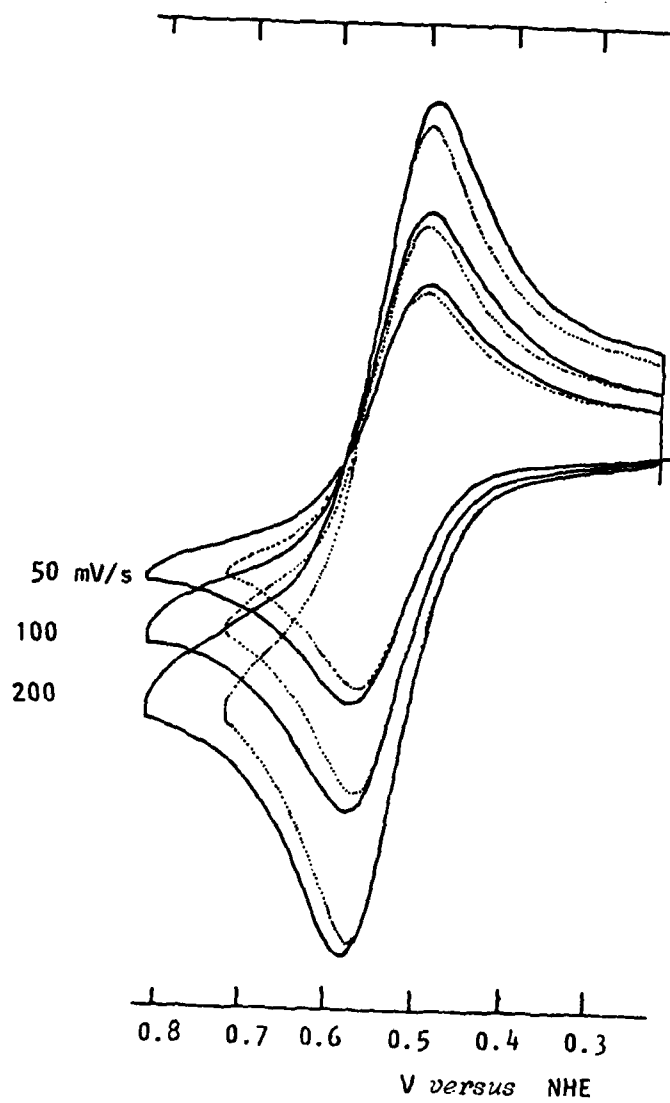


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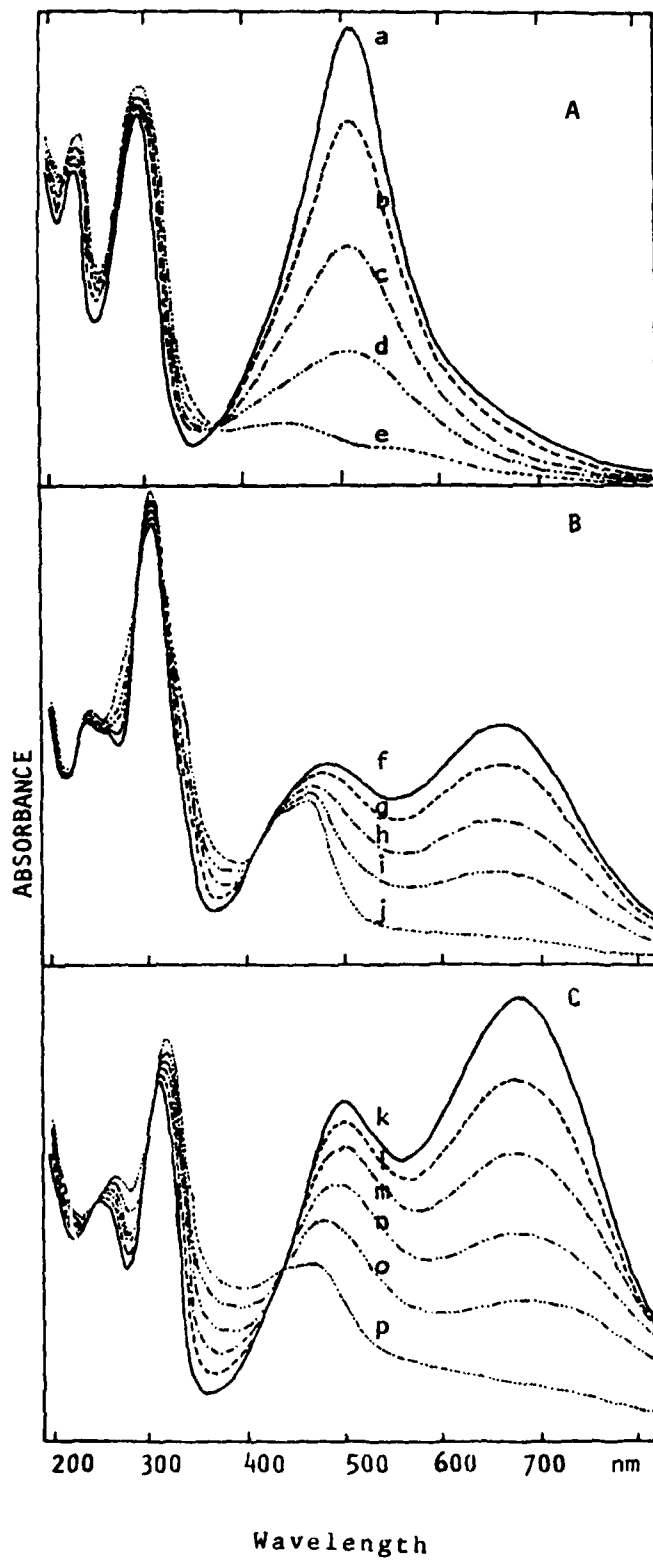


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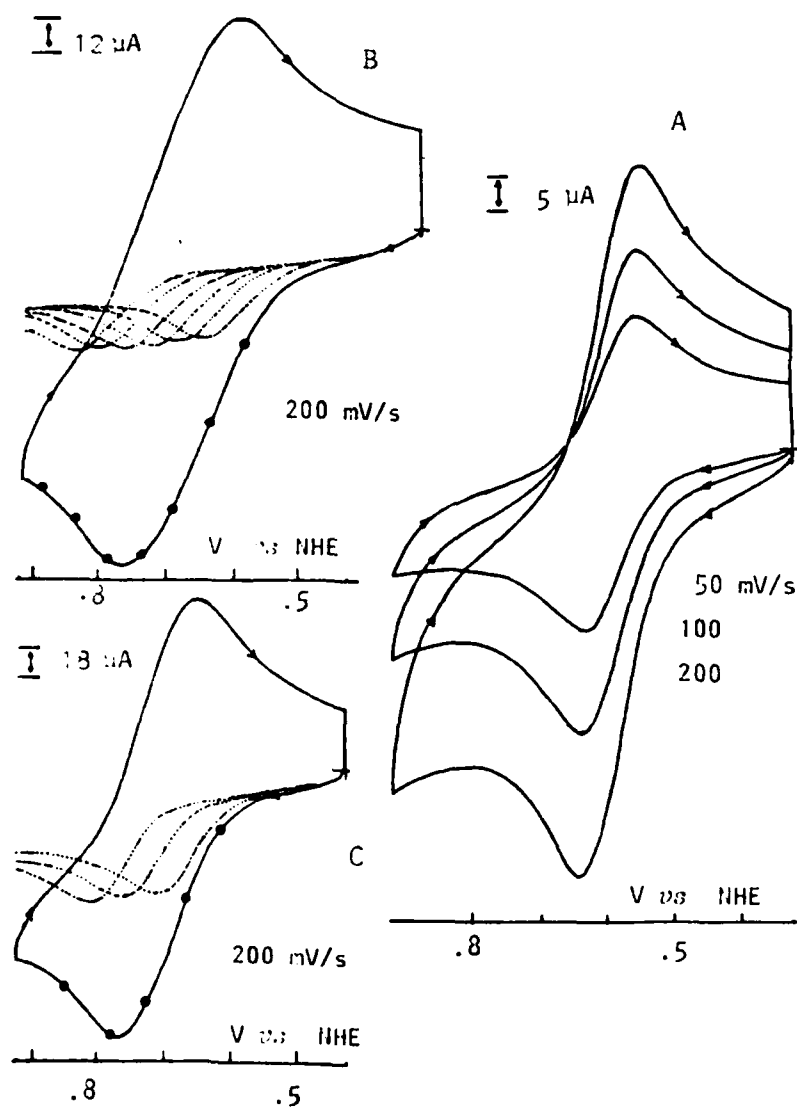


Fig. 8

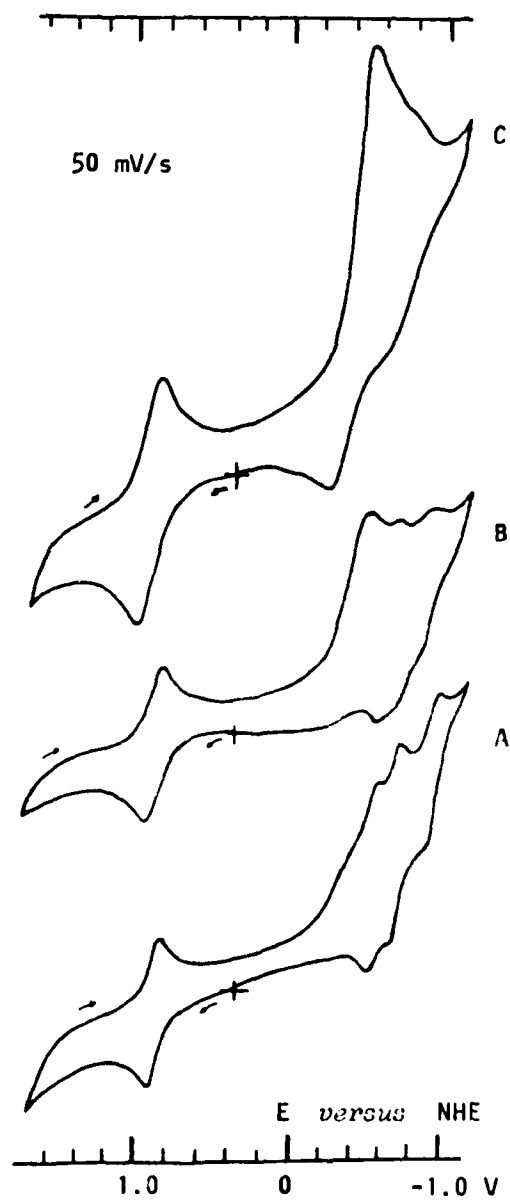


Figure 1

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